

## REMARKS

Claims 1-12 are pending in the present application. Reexamination of the application and reconsideration of the rejections and objections are respectfully requested in view of the following remarks, which follow the order set forth in the Office Action ("the Action").

### *Claim Objections*

Claim 1 is objected to because allegedly an acronym is used therein without first being defined. Applicants submit that the meaning of the term "NASICON" is commonly known to one of ordinary skill in the art and thus there is no need to further define the term. The term NASICON is used frequently in patent references related to rechargeable Li batteries. For example, U.S. Patent No. 5,910,382, which is incorporated by reference in the present application, defines NASICON as "an acronym for the framework host of a sodium superionic conductor  $\text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3$ . The compound  $\text{Fe}_2(\text{SO}_4)_3$  has two forms, a rhombohedral NASICON structure and a related monoclinic form." *Col. 10, lines 43-46*. In addition, Applicants are providing a copy of a 2005 publication in Geophysical Research Abstracts, Vol. 7, 02000, 2005, that confirms the definition incorporated in the present application and explains that NASICON is an established term covering crystalline phosphates of transition metals having a known formula. *Geophysical Research Abstracts, par. 1*. The above-referenced article is attached as Appendix A. Based on the foregoing, Applicants request reconsideration and withdrawal of the instant objection.

### *Rejection under 35 U.S.C. § 102(b)*

Claims 1, 4, 7, and 12 are rejected under 35 U.S.C. § 102(b) as allegedly being anticipated by Huang et al., "Approaching theoretical capacity of  $\text{LiFePO}_4$  at room temperature at high rates;" *Electrochemical and solid state letters*, vol. 4, no. 10, October 2001 ("Huang"). Applicants traverse the rejection.

Claim 1 recites a process for preparing a carbon-coated, Li-containing olivine or NASICON powder. The process includes preparing a water-based solution including, as solutes, one or more Li-containing olivine or NASICON precursor compounds and one or more carbon-bearing monomer compounds. It further includes precipitating the Li-containing olivine or NASICON precursor compounds and polymerizing the monomer compounds in a single step. The process also includes heat treating the obtained precipitate

in a neutral or reducing environment in order to form a Li-containing olivine or NASICON crystalline phase and decompose the polymer to carbon.

Huang discloses preparation of  $\text{LiFePO}_4/\text{C}$  composites using two methods, so-called methods A and B. *p. A170, ¶ 3*. Method A involved solid state mixing following by firing. Specifically, three solid salts,  $\text{CH}_3\text{COOLi}$ ,  $(\text{CH}_3\text{COO})_2\text{Fe}$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$ , were mixed together with a carbon gel, which was formed from the polymerization of resorcinol-formaldehyde. *p. A170, ¶ 3*. Importantly, the carbon gel formation took place *prior* to the gel being mixed with any materials containing Li, Fe, or  $\text{PO}_4$ . Further, method A disclosed *no* precipitation. Rather, method A disclosed mixing salts in a solid state with a carbon gel. In this regard, Huang states that the organic precursor was chosen because it provided “a facile method of contacting the carbon with the solid state mixture.” *p. A172, ¶ 1*.

Method B involved mixing surface oxidized carbon black with  $\text{LiCl}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{H}_3\text{PO}_4$  in water. The water was then evaporated in an inert atmosphere, and the mixture was heat treated. However, method B disclosed no evaporation of water from a *precipitated mixture* at the *claimed temperature*. Further, method B disclosed no precipitation and no polymerization whatsoever, much less polymerization and precipitation in a single step.

A claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference. Applicants submit that Huang fails to disclose, either implicitly or explicitly, each and every element of claim 1. Claim 1 requires *precipitating* the Li-containing olivine or NASICON precursor compounds *and polymerizing* the monomer compounds in a *single step*. As discussed above, in method A, Huang fails to disclose precipitating of any sort. As discussed above, method B fails to disclose precipitating of any sort and fails to disclose polymerizing of any sort. In contrast, the present claims require precipitating and polymerizing in a single step. Based on the foregoing, Applicants assert that Huang fails to anticipate claim 1, and respectfully request reconsideration and withdrawal of the instant rejection.

### ***Rejections under 35 U.S.C. § 103(a)***

Claims 2-3 are rejected under 35 U.S.C. §103(a) as being allegedly unpatentable over Huang in view of Armand et al., WO/0227823 (“Armand”). Applicants traverse this rejection. As discussed in detail above, Huang discloses preparation of  $\text{LiFePO}_4/\text{C}$  composites using two different methods. Neither method discloses precipitation of a

precursor compound of any sort. Further, Huang fails to teach or suggest a process wherein precipitating and polymerizing occur in a single step as required in claim 1.

Armand discloses a method of synthesizing compounds of the formula  $C-Li_xM_1-yM'(XO_4)_n$  wherein: x, y, and n represent numbers such that  $0 \leq x \leq 2$ ,  $0 \leq y \leq 0.6$ , and  $1 \leq n \leq 1.5$ ; M is a transition metal or a mixture of transition metals of the first line of the periodic table; M' is an element with fixed valency selected among  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Al^{3+}$ ,  $Zn^{2+}$ , or a combination of said elements; and X is selected among S, P, and Si. Armand fails to disclose or suggest x being 1, 2, or 3 or X being  $P_{x-1}S_x$  with  $0 \leq x \leq 1$  as recited in claim 2. Rather, Armand teaches a composition wherein Li may or may not be present and X is selected from S, P, and Si. In contrast, Li is a required element in the recited crystalline phase of claim 2. One of ordinary skill would not be directed to a composition wherein Li is required and wherein X is a combination of elements as recited in claim 2 by Armand.

Combining the disclosure of Armand with the disclosure of Huang fails to overcome the deficiencies present in the Huang reference. As such, Applicants assert that Huang in combination with Armand fails to make obvious the invention of claim 2, and thus necessarily claim 3, which depends from claim 2. Accordingly, Applicants respectfully request reconsideration and withdrawal of the instant rejection.

Claims 5-7 are rejected under 35 U.S.C. §103(a) as being allegedly unpatentable over Huang in view of Pechini, U.S. Patent No. 3,330,697 ("Pechini") and Tietz et al., WO 02/44103 ("Tietz"), and claim 8 is rejected as being allegedly unpatentable over Huang in view of Pechini, Tietz, and Wurm et al., WO 02/099913 ("Wurm"). Applicants traverse this rejection.

As discussed in detail above, Huang discloses preparation of  $LiFePO_4/C$  composites using two different methods. Neither method discloses precipitation of a precursor compound of any sort. Further, Huang fails to teach or suggest a process wherein precipitating and polymerizing occur in a single step as required in claim 1. Combining the disclosures of Pechini, Tietz, and Wurm with the disclosure of Huang fails to overcome the deficiencies present in the Huang reference. As such, Applicants assert that Huang in combination with Pechini, Tietz, and Wurm fails to make obvious the inventions of claims 5-8. Accordingly, Applicants respectfully request reconsideration and withdrawal of the instant rejection.

Claims 9-11 are rejected under 35 U.S.C. §103(a) as being allegedly unpatentable over Huang in view of Ravet et al., U.S. Patent Publication No. 2002/0195591 ("Ravet").

Claims 9-11 each recite carbon-coated  $\text{LiFePO}_4$  for use in Li insertion-type electrodes. As recited in claim 9, when  $\text{LiFePO}_4$  is used as an active component in a cathode that is cycled between 2.0 and 4.5 V against a Li anode at a discharge rate of  $C/5$  at 25 °C, it can be characterized by a reversible electrode capacity expressed as a fraction of the theoretical capacity and a total carbon content of at least 75% capacity and less than 4 wt.% carbon, or, at least 80% capacity and less than 8 wt.% carbon.

The Office Action asserts that Huang fails to disclose a carbon content less than 4 wt.%. In fact, Huang discloses a carbon content of 20wt.% in all cases. *p. A171, ¶1*. The Office Action cites Examples 1, 2, and 3 of Ravet for teaching a carbon-coated  $\text{LiFePO}_4$  electrode material for a battery with less than 4wt.% carbon and having over 75% capacity of the theoretical capacity. Despite the assertion of the Office Action, Applicants submit that claims 9-11 are not obvious over of Huang in view of Ravet.

To establish a *prima facie* case of obviousness, first, there must be some suggestion or motivation, either in the references themselves or in the knowledge in the art, to modify the reference or to combine reference teachings; second, there must be a reasonable expectation of success *and* third, all claim limitations must be considered. *See* MPEP § 2143. Applicants respectfully submit that the Office Action has not considered every limitation as required by the third criterion above.

Specifically, Applicants submit that the Office Action has failed to consider the limitation of 25°C, i.e., room temperature. Electrochemical testing in Examples 1, 2, and 3 of Ravet is primarily performed at a temperature of 80°C. Results from tests performed at 80°C cannot be fairly compared with tests performed at room temperature because high temperatures enhance lithium diffusion rate thus leading to increased capacities. The concept of increased lithium diffusion rate at increased temperatures is known to one of ordinary skill in the art. Applicants have attached an article entitled "Thermal Stability of  $\text{LiFePO}_4$ -Based Cathodes," *Electrochemical and Solid-State Letters*, 3(2) 66-68 (2000), to support Applicants' assertion regarding lithium diffusion rates, as Appendix B. Applicants direct the Examiner's attention to pg. 66, ¶ 4 for support of Applicants' assertion. Thus, one of ordinary skill in the art would not expect that the discharge rate of Ravet would hold at 25°C.

For the one test in Ravet performed at room temperature, carbon black and EPDM were added to the  $\text{LiFePO}_4$  in a ratio of 85:5:10. Such addition of carbon inevitably results in a carbon content of greater than 8wt.%. Consequently, the basis put forth in the Office Action for citing Ravet, i.e., a carbon-coated  $\text{LiFePO}_4$  electrode material for a battery with

less than 4wt.% carbon and having over 75% capacity of the theoretical capacity is lost. Further, the battery prepared with this material has low power ( $\eta$ [[0065]]), which would not direct one of ordinary skill in the art to further modify this battery as suggested in the Office Action.

Applicants assert that one of ordinary skill in the art reviewing Huang in view of Examples 1, 2, and 3 of Ravet would not find the invention of claims 9-11 to be obvious. Rather, one of ordinary skill would likely find the invention of claims 9-11 to be unexpected because the claimed  $\text{LiFePO}_4$  is able to maintain a high electrode capacity with low carbon content and at room temperature. As such, Applicants respectfully request reconsideration and withdrawal of the instant rejection.

For the foregoing reasons, independent claims 1, 9, 10, and 11 and claims 2-8 and 12 depending therefrom are considered to be allowable. A Notice to this effect is respectfully requested. If any questions remain, the Examiner is invited to contact the undersigned at the number given below.

Respectfully submitted,

HUTCHISON LAW GROUP PLLC

Date:

July 11, 2008

By:

Allyn B. Rhodes

Allyn B. Rhodes

Registration No. 56,745

P.O. Box 31686  
Raleigh, NC 27612  
+1.919.829.9600

## **EXHIBIT A**



## **Disorder and mobility of lithium ions in NASICON phosphates for energy applications**

**M. Catti**

Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, Milano, Italy  
(catti@mater.unimib.it)

NASICON materials are crystalline phosphates of transition metals Me and alkali atoms A (Li or Na), according to the formula  $A_x\text{Me}_2(\text{PO}_4)_3$ , which display a high mobility of the  $A^+$  ion, and are thus promising materials for applications in rechargeable lithium batteries. They may be used as solid state electrolytes or as electrodes, according to the value of the redox standard potential of the transition metal cation. The structural characterization of the mobile alkali ion environment, and of its bonding interactions with the neighbouring atoms, is essential to understand the mechanisms of ionic conduction in these phases. Owing to the poor X-ray scattering power of lithium, neutron scattering is a particularly suitable technique for such studies. We have been investigating a number of lithium NASICON compounds by high-resolution neutron powder diffraction at variable temperature (HRPD time-of-flight diffractometer at the ISIS Facility, Rutherford Appleton Laboratory, U.K.; resolution  $\Delta d/d \approx 4 \times 10^{-4}$ ). By use of Rietveld refinements coupled with difference Fourier maps, multiple disorder effects involving the alkali ions in the large M1 and M2 cavities of the NASICON framework can be detected [1-5].

The standard NASICON structure is rhombohedral  $R\bar{3}c$ , and may be derived from the corundum ( $\text{Al}_2\text{O}_3$ ) structure by the Al/Me substitution and by replacing every O atom with a  $\text{PO}_4$  group. There is thus a framework of  $\text{MeO}_6$  octahedra and  $\text{PO}_4$  tetrahedra linked to one another, where two large cavities are observed, surrounding the M1 (at 0,0,0 with  $\bar{3}$  symmetry) and M2 (at  $2/3, 0, 1/4$  with 2 symmetry) sites, respectively. The alkali ions are therein located with variable degree of order/disorder, and the channels connecting such cavities provide the mobility paths for ionic transport under an applied electric field. Structural distortions involving a symmetry lowering

to orthorhombic, monoclinic or triclinic are possible, and they may affect the disorder state and mobility of lithium substantially.

The most important systems examined were  $\text{LiZr}_2(\text{PO}_4)_3$ ,  $\text{Li}_{1+x}\text{Fe}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (with  $0.5 < x < 1.2$ ),  $(\text{Li,Na})_2\text{FeTi}(\text{PO}_4)_3$ , and  $(\text{Li,Na})_2\text{FeZr}(\text{PO}_4)_3$ . They correspond to different variants of the basic NASICON structure, with space groups  $R\bar{3}c$ ,  $R\bar{3}$ ,  $\text{Pbna}$ ,  $\text{Pbca}$ ,  $C\bar{1}$ . The lithium atoms appear to be distributed over different sites located in the M1 and/or M2 main hollows, with a variable extent of disorder. A detailed analysis of such sites allowed us to identify the pathways of ion transport inside the NASICON framework, and then to propose atomistic mechanisms to explain the macroscopic properties of ionic conductivity in these systems.

- [1] M. Catti and S. Stramare, Solid State Ionics 136-137, 489 (2000)
- [2] M. Catti, N. Morgante and R.M. Ibberson, J. Solid State Chem. 152, 340 (2000)
- [3] M. Catti, J. Solid State Chem. 156, 305-312 (2001)
- [4] M. Catti, A. Comotti and S. Di Blas, Chem. Materials 15, 1628 (2003)
- [5] M. Catti, A. Comotti, S. Di Blas and R.M. Ibberson, J. Mater. Chem. 14, 835 (2004)



## **EXHIBIT B**

Thermal Stability of  $\text{LiFePO}_4$ -Based CathodesAnna S. Andersson,<sup>a,\*</sup> John O. Thomas,<sup>a,\*\*</sup> Beata Kalska,<sup>b</sup> and Lennart Haggström<sup>b</sup><sup>a</sup>Department of Inorganic Chemistry and <sup>b</sup>Department of Physics, Ångström Laboratory, Uppsala University, SE-751 31 Uppsala, Sweden

The capacity and cyclability of solid-state synthesized  $\text{LiFePO}_4$ -based laminate cells of type  $\langle \text{Li} | \text{liq. el.} | \text{LiFePO}_4 \rangle$  have been studied at 23, 40, and 60°C. Larger capacities were obtained for cells cycled at the elevated temperatures. No evidence was found of potentially troublesome reactions between the different components of the cells under charged and discharged conditions up to 85°C. Resonant X-ray diffraction peaks were observed from the delithiated  $\text{FePO}_4$ /heterosite phase for cells cycled at ambient temperature. Mössbauer spectroscopy showed different residual amounts of  $\text{Fe}^{3+}$  at the different temperatures: 22, 7, and 8% at 23, 40, and 60°C, respectively. The amount of residual  $\text{Fe}^{3+}$  was thus largest for cells cycled at room temperature, suggesting that slow kinetics hinder effective lithium insertion.

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Advanced lithium/lithium-ion polymer batteries have a wide range of applications in electronic devices and future electric vehicle systems. The high-temperature behavior of the constituents of such a battery is a vital issue, because it can be heated inadvertently, or be used in elevated-temperature applications. Thermal stability studies of  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiMn}_2\text{O}_4$  with varying lithium content have shown  $\text{LiMn}_2\text{O}_4$  spinel to be the most stable<sup>1</sup> but, in spite of this, corrosion of the spinel related to the disproportionation of  $\text{Mn}^{3+}$  into  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$  remains a severe problem.<sup>2</sup> A recent study has confirmed that capacity loss in the spinel system is due, at least in part, to the formation of a less chemically active (with respect to lithium insertion) protonated phase of  $\lambda\text{-MnO}_2$  upon storage in the electrolyte.<sup>3</sup>

An iron-based cathode would be ideal, from both economic and environmental viewpoints, and several iron-based compounds have been investigated as cathodes in secondary lithium cells. Indeed, much effort has been put into finding an Fe-analog to the layered systems  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$ . Layered  $\text{LiFeO}_2$  has been prepared by ionic exchange of  $\alpha\text{-NaFeO}_2$  in molten salts, though attempts to delithiate this phase are not yet successful.<sup>4,5</sup> Currently, four structural modifications of  $\text{LiFeO}_2$  are known to insert/extract lithium reversibly, i.e., a corrugated-layer type,<sup>5,7</sup> a goethite-type,<sup>7</sup> a tunnel structure,<sup>8</sup> and a low-temperature  $\alpha$ -phase.<sup>9</sup> The orthorhombic corrugated-layer type  $\text{LiFeO}_2$ , obtained by ion exchange of  $\gamma\text{-FeOOH}$  with  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,<sup>5,6</sup> or with lithium alkoxide,<sup>7</sup> has a capacity of 100 mAh/g after 10 cycles between 1.5 and 4.5 V.<sup>7</sup> However, all  $\text{LiFeO}_2$  modifications exhibit a sloping discharge/charge curve and a rather low average voltage v.s.  $\text{Li/Li}^+$ , which is not optimal for battery applications. An  $\text{FeOOH}$  with a tunnel-type structure (the  $\beta$ -phase) has been prepared by hydrolysis of  $\text{FeCl}_3\cdot\text{H}_2\text{O}$  in water; initial studies show a reversible capacity of 275 mAh/g at an average voltage of 2.3 V.<sup>10</sup> Prussian blue, a mixed-valence iron hexacyanometalate containing water of crystallization, has recently been reported to cycle reversibly at 3 V.<sup>11,12</sup>

A series of lithium-containing compounds incorporating large polyanions,  $\text{XO}_4^{3-}$  for  $\text{X} = \text{S}, \text{P},$  and  $\text{As}$ , has recently been investigated;<sup>13-19</sup> most notably, the rhombohedral modifications of  $\text{Fe}_2(\text{SO}_4)_3$ ,<sup>13,14</sup> and  $\text{Li}_2\text{Fe}_2(\text{PO}_4)_3$ ,<sup>18</sup> and orthorhombic  $\text{LiFePO}_4$ .<sup>15,16</sup> The large polyanions appear to stabilize the structure and "trap" the Fe ions.  $\text{LiFePO}_4$  with a theoretical capacity of 170 mAh/g, compared to 148 mAh/g for  $\text{LiMn}_2\text{O}_4$ , emerges as a most promising candidate as cathode material for low-power, rechargeable lithium-ion polymer batteries. It is inexpensive, nontoxic, easy to handle (i.e., nonhygroscopic) and environmentally friendly.  $\text{LiFePO}_4$  has an ordered olivine structure (Fig. 1), in which  $\text{FeO}_6$  octahedra share common corners in the  $bc$  plane.<sup>20,21</sup>

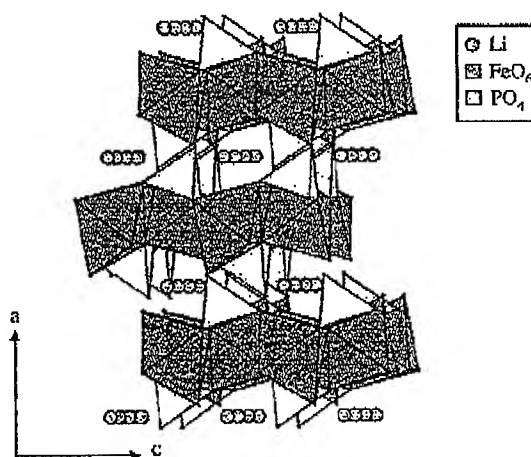


Figure 1. The structure of  $\text{LiFePO}_4$  (olivine) viewed along the  $b$  axis. The P atoms occupy tetrahedral sites; the Li and Fe atoms occupy octahedral sites.

It has been shown that  $\text{LiFePO}_4$  cycles well at ambient temperature. However, a reversible capacity loss occurs at higher current densities, which could be due to limiting "interface diffusion" within a single grain.<sup>15</sup> This limitation should be less serious in a high-temperature application. Elevated temperatures will enhance the lithium diffusion rate and could therefore increase the reversible capacity at higher current densities. However, it is not only the lithium diffusion rate which increases at higher temperatures, but also a number of other less desirable reactions. It is therefore critically important to probe the stability of different electrode/electrolyte combinations.

The oxidation of  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$  for  $\text{Mn}/(\text{Fe}+\text{Mn}) = 0.21$  and 0.71 has been investigated in the temperature range 20–900°C.<sup>22,23</sup> Padhi *et al.*<sup>15</sup> have investigated the thermal stability of  $\text{FePO}_4$  by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA); no appreciable weight change occurred on thermal treatment in an  $\text{N}_2$  atmosphere up to 350°C. The DSC curves showed a reversible transition at 300°C, the origin of which is unknown. TGA measurements made in oxygen atmosphere exhibited a similar weight loss behavior.

In this paper, we examine the thermal stability of  $\text{LiFePO}_4$  in its charged and discharged states in the presence of different electrolyte combinations and the effect of temperature on its structure and cycling performance.

## Experimental

$\text{LiFePO}_4$  was prepared by the solid-state reaction of  $\text{Li}_2\text{CO}_3$  (≥99% Merck),  $\text{Fe}(\text{II})\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$  (99%, Riedel-Hahn) and  $(\text{NH}_4)_2\text{HPO}_4$

\* Electrochemical Society Student Member.

\*\* Electrochemical Society Active Member.

E-mail: josh.thomas@kemi.uu.se

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67

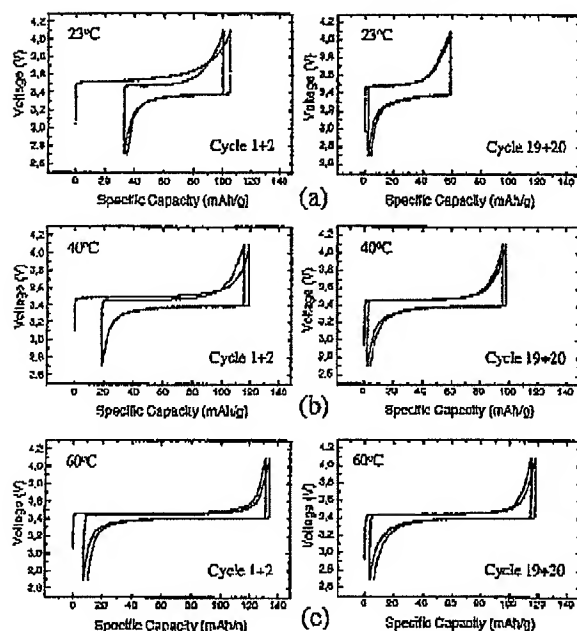


Figure 2. Typical charge/discharge curves for  $\text{LiFePO}_4$  at (a) 23, (b) 40, and (c) 60°C. For clarity, only the first two and last two cycles are shown. Cutoff voltages were 2.7 and 4.1 V, and the current density was 23 mA/g.

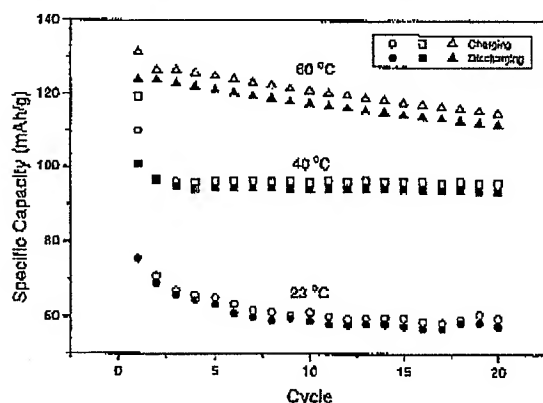


Figure 3. Capacity of  $\text{LiFePO}_4$  vs. cycle number at 23, 40, and 60°C. Cutoff voltages were 2.7 and 4.1 V; current density was 23 mA/g.

(≥99%, Merck).<sup>24</sup> The starting materials were handled in an Ar glove box (<3 ppm  $\text{H}_2\text{O}/\text{O}_2$ ) to avoid oxidation. The synthesis was performed in three consecutive steps; before each step, the material was ground and mixed thoroughly. The starting materials were first heated slowly to 300°C in vacuum to "predecompose" the oxalate and phosphate. The powder was then coated with *n*-hexane to prevent oxidation, and transferred to another furnace, where it was heated to 450°C under a flow of  $\text{N}_2$  gas, and maintained at this temperature for 10 h. After grinding and homogenizing, the sample was pressed into pellets ( $\phi = 12$  mm,  $P = 1.5$  ton), annealed at 800°C ( $\text{N}_2$  atmosphere) for 36 h, and allowed to cool slowly to room temperature. The pellets were then ground in a planetary ball mill.

The phase-purity of the material was ascertained initially by X-ray diffraction (XRD) using a Guinier-Hägg powder camera. Films were evaluated with an LS-18 line scanner. Silicon was added as an internal standard to facilitate cell parameter determination. The lines were

indexed and refined using an indexing/refinement routine supplied by STOE & Cie. The orthorhombic cell parameters obtained were  $a = 10.3300(7)$ ,  $b = 6.0063(6)$ , and  $c = 4.6909(4)$  Å. Space group:  $Pnma$ .

The electrochemical performance of the materials was studied in "coffee-bag" type cells. Cathodes were prepared by spreading a mixture of  $\text{LiFePO}_4$ , Shawinigan black (SB) carbon powder, and ethylene propylene diene terpolymer (EPDM) rubber binder (ratio 80:15:5) in cyclohexane onto an Al-foil current collector covered with a thin coating of CL51 (a suspension of fine carbon particles in an organic binder). The electrodes were dried overnight in air at 60°C, cut into 3.1  $\text{cm}^2$  disks, and dried again at 120°C in vacuum. The typical  $\text{LiFePO}_4$  loading for each cathode was 16–18  $\text{mg}/\text{cm}^2$ . Half-cells were also assembled in the Ar-filled glove box; the cathode was laminated with a glass-wool or Solupor separator soaked in electrolyte and pressed onto a lithium-foil counter electrode. The laminates were packed in polymer-coated aluminum bags (coffee-bags), evacuated, and sealed. The solvents used were of Selectipur quality from Merck.

Cells were cycled galvanostatically 20 times between 2.7 and 4.1 V (23 mA/g) at room temperature, 40, and 60°C using a Digatron battery test system BTS-600. The electrolyte used for the electrochemical studies was 1 M  $\text{LiBF}_4$  (Tomiyama) in ethylene carbonate/dimethyl carbonate (EC/DMC) 2:1.

After the cycling, XRD measurements were performed on the cells using an automatic STOE & Cie GmbH STADI powder diffractometer equipped with a small, straight-wire position sensitive detector ( $\sim 5^\circ$  in  $2\theta$ ). Exposures were made in transmission mode with Ge-monochromatized  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 1.540598$  Å) using a specially designed battery holder for *in situ* measurements<sup>25</sup> to facilitate oscillation of the cells.

The Mössbauer measurements on cycled cathodes were made using a 512-channel Mössbauer spectrometer working in constant acceleration mode with a  $^{57}\text{CoRh}$  source. The Mössbauer spectra in transmission geometry were collected together with the calibration spectrum of  $\alpha\text{-Fe}$  foil at room temperature. The Fe content of each cathode was ca. 2  $\text{mg}/\text{cm}^2$ . The cathodes were enclosed in polymer-coated aluminum coffee bags; each spectrum contained a doublet (intensity 5%) originating from the Fe impurity in the Al foil.

Thermal analyses were performed on a Mettler TA4000 heat-flow DSC. Small pieces of the cathode ( $\phi = 5$  mm), both discharged and charged, were placed together with separators soaked in electrolyte in Al pans, which were sealed in the Ar glove box. Thermal scans were made between 30 and 85°C at a heating rate of  $1^\circ\text{C}/\text{min}$ .

## Results and Discussion

**Thermal stability.**—The salts studied were  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ , and  $\text{LiPF}_6$  in combinations with 1 M EC/propylene carbonate (PC) 2:1 (not for  $\text{LiPF}_6$ ) and EC/DMC 2:1; no significant features were observed in the DSC curves for any of these salt/solvent combinations together with  $\text{LiFePO}_4$  in the temperature range room temperature to 85°C; no salt type would seem to be superior to any other from a thermal stability standpoint.

**Electrochemistry.**—The cycling behavior of the material is strongly dependent on temperature (Fig. 2 and 3). At room temperature, the first charge capacity is typically 90–100  $\text{mAh}/\text{g}$ ; a large capacity loss (40–50  $\text{mAh}/\text{g}$ ) occurs during the first few cycles. The remaining capacity is maintained up to the twentieth cycle. At 40°C, the charge capacity is initially 100–120  $\text{mAh}/\text{g}$ , decreasing to ca. 95  $\text{mAh}$  by the twentieth cycle. At 60°C, the charge capacity decreases slowly from 130  $\text{mAh}/\text{g}$  for the first cycle to 115  $\text{mAh}/\text{g}$  for the twentieth cycle. The discharge capacity also increases with the temperature, but not as much as the charge capacity; the difference between the charge and discharge capacities after the first cycle is seen to increase with temperature.

The general appearance of the voltage curves (Fig. 2) is also different at different temperatures. The plateau potentials of the charge and discharge curves differ by  $\sim 0.2$  V at room temperature and by  $\sim 0.1$  V at 60°C, indicating that polarization effects are less pronounced at the higher temperature.

Table I. Mössbauer parameters for discharged  $\text{LiFePO}_4$  cathode material after 20 cycles at different temperatures. CS: centroid shift;  $\Delta E_Q$ : electric quadrupolar splitting.

Sample	Intensity (%)	$\text{Fe}^{2+}$		Intensity (%)	$\text{Fe}^{3+}$	
		CS (mm/s)	$\Delta E_Q$ (mm/s)		CS (mm/s)	$\Delta E_Q$ (mm/s)
As made	100	1.220(5)	2.963(5)	0	-	-
After 20 cycles at 23°C	78(1)	1.222(5)	2.963(5)	22(1)	0.433(5)	1.495(5)
After 20 cycles at 40°C	92(1)	1.226(5)	2.963(5)	7(1)	0.435(5)	1.477(5)
After 20 cycles at 60°C	93(1)	1.223(5)	2.963(5)	8(1)	0.436(5)	1.459(5)

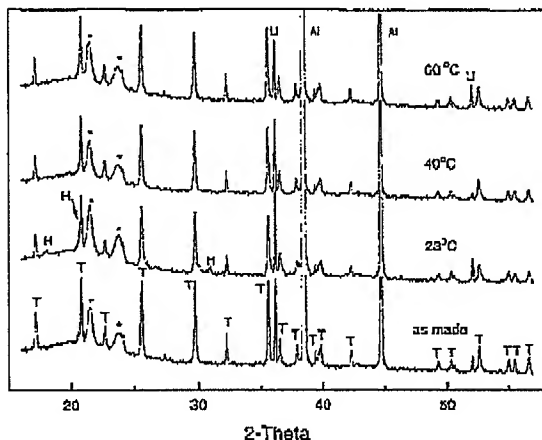


Figure 4. X-ray diffractograms from half-cells: as made, and after 20 cycles at 23, 40, and 60°C. T:  $\text{LiFePO}_4$  (triphylite); H:  $\text{FePO}_4$  (heterosite); asterisks (\*) mark peaks from the polymer in the packaging.

**Mössbauer spectroscopy.**—The parameters obtained from fitting the Mössbauer data are given in Table I. All hyperfine parameters are in good agreement with our earlier observed values for a  $< \text{Li-metal}$  liq.  $\text{eLiLiFePO}_4$  cell.<sup>26</sup> The amount of residual  $\text{Fe}^{3+}$  is, in each case, in good agreement with that expected from the observed capacity loss during the first cycle. At room temperature, this is 35 mAh/g, which would correspond to a remnant  $\text{Fe}^{3+}$  content of ca. 20%; the value obtained from Mössbauer spectroscopy is 22%.

At 40°C, the capacity loss during the first cycle is 20 mAh/g, i.e., 11%; the corresponding value from Mössbauer spectroscopy is 7%. At 60°C, there is only a very small decrease in capacity during the first cycle and, even if there is a continuous slow decrease in capacity up to the twentieth cycle, the total capacity loss is still not more than 10 mAh/g, which corresponds to ca. 6% remnant  $\text{Fe}^{3+}$ . The Mössbauer data gives 8%.

**XRD.**—The X-ray diffractograms for cells cycled at room temperature (23°C), 40, and 60°C are very similar to those obtained for a cell "as made" (Fig. 4). In all diffractograms, sharp intense peaks can be observed from the aluminum current collector and the lithium-metal anode. Two somewhat broader peaks occur at 21.4 and 23.8° in  $2\theta$  originating from the polymer component in the coffee bag. In the diffractogram for the cell cycled 20 times at room temperature, there are two small peaks belonging to the heterosite phase. This would suggest that lithium insertion is impeded by slow kinetics at the lower temperatures, thus preventing the complete reduction of  $\text{Fe}^{3+}$ .

### Conclusions

This pilot study has shown that  $\text{LiFePO}_4$  is worth looking at more closely as a viable candidate for lithium/lithium-ion polymer battery applications; its capacity improved at slightly elevated temperatures, and no evidence of potentially troublesome reactions could be

observed. Moreover, the cycling capacity would appear to be constant at 40°C at least over the first 20 cycles. At 60°C, the performance deteriorates slowly over the first 20 cycles; this can indicate that the working temperature for this type of cell may be restricted to somewhere below 60°C. This temperature is presumably dependent on subtleties in particle morphology and size distribution, however. More extended cycling tests must be made to shed further light on the more long-term performance of this material. The parameters used in this present study are by no means optimized.

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